

REMARKS/ARGUMENTS

Claims 1-9 are pending herein. Claims 1-8 have been amended hereby to correct matters of form and for clarification purposes only. New claim 9 has been added hereby. Applicants respectfully submit that support for new claim 9 can be found, for example, on page 17 of the substitute specification submitted herewith. Applicants respectfully request that no new matter has been added.

1. Applicants again affirm the provisional telephone election made with traverse on May 9, 2005 to prosecute claims 1-5 and 8, and acknowledge that claims 6 and 7 have been withdrawn as being drawn to a non-elected invention.

2. Claims 1-5 and 8 were rejected under the judicially created doctrine of obviousness-type double patenting over claims 1-4 of U.S. Patent No, 6,936,560. Applicants respectfully traverse this rejection.

Applicants respectfully submit that the PTO has mischaracterized the content of claims 1-4 of the '560 patent (see page 4 of the Office Action). That is, the claims of the '560 patent recite that the porous substrate has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ (molar ratio) of 40 to less than 200. The claims of the '560 patent do not, however, recite anything about the $\text{SiO}_2/\text{Al}_2\text{O}_3$ (molar ratio) of the separation membrane (as presently claimed).

For at least the foregoing reasons, Applicants respectfully request that the above rejection be reconsidered and withdrawn.

3. Claims 1-5 and 8 were rejected under §103(a) over Lai. Applicants respectfully traverse this rejection.

Independent claim 1 recites a laminated zeolite composite comprising a MFI membrane comprising a MFI type zeolite and having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ (molar ratio) of 40 to 100, and a porous substrate comprising a MFI type zeolite and having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ (molar ratio) of 20 to 400, wherein the MFI membrane is formed on the porous substrate.

The PTO admitted that Lai “does not explicitly disclose the silica to alumina molar ratio” (Office Action, page 6, lines 2-3), but asserted that “such features are properties which can be easily determined by one of ordinary skill in the art” (Office Action, page 6, lines 3-4). The PTO also asserted that it would have been obvious to modify this otherwise undisclosed feature by routine experimentation. Applicants respectfully disagree.

First, the claimed $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios are not properties—they are compositional features of the present invention. Moreover, even if, *arguendo*, the claimed molar ratios could be "easily determined" by one of ordinary skill in the art, the fact remains that Lai is completely silent with respect to these claimed features. Still further, Applicants respectfully submit that there is no disclosure or suggestion in Lai that the otherwise undisclosed $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios are in any way result effective parameters, with respect to either a membrane or a substrate. Whether one skilled in the art could have "possibly" arrived at the claimed ratios does not render the undisclosed ratios obvious in view of Lai, particularly when Lai is also silent as to whether the otherwise undisclosed feature is a result effective parameter. For at least the foregoing reasons, Applicants respectfully submit that the PTO has not established a *prima facie* case of obviousness.

Notwithstanding the above, Applicants respectfully submit that the present specification includes data that specifically shows that unexpected results are attributed to the claimed $\text{SiO}_2/\text{Al}_2\text{O}_3$ (molar ratios), particularly with respect to the claimed MFI membrane. For example, Applicants respectfully submit that the specification demonstrates a correlation between the $\text{SiO}_2/\text{Al}_2\text{O}_3$ (molar ratio) in the MFI membrane and the gas separation characteristics that has not been recognized prior to the present application.

That is, Table 3 of the present specification shows that the separation factor for butane isomers that are supplied to laminated zeolite composites according to the present invention is significantly higher, and that cracks are not present at the surface of the MFI membrane, when the $\text{SiO}_2/\text{Al}_2\text{O}_3$ (molar ratio) of the MFI membrane is

within the range recited in independent claim 1 (Example 1 and Example 2). Example 1 shows a separation factor of 84.3 when the $\text{SiO}_2/\text{Al}_2\text{O}_3$ (molar ratio) of the membrane was 52, and Example 2 shows a separation factor of 62.0 when the $\text{SiO}_2/\text{Al}_2\text{O}_3$ (molar ratio) of the membrane was 79.

On the other hand, samples having MFI membranes with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ (molar ratio) that was outside the claimed range of 40-100 (either higher or lower), had significantly lower separation factors of less than 20, and moreover, cracks were observed when the $\text{SiO}_2/\text{Al}_2\text{O}_3$ (molar ratio) was less than 40 (see Table 3).

In view of the above, Applicants respectfully submit that it would not have been obvious for one of ordinary skill in the art to have modified features (i.e., the claimed molar ratios) that are simply not disclosed or suggested in Lai. Moreover, since Lai does not disclose or even remotely suggest that the undisclosed molar ratios are result effective parameters, Applicants respectfully submit that the claimed $\text{SiO}_2/\text{Al}_2\text{O}_3$ (molar ratio) ranges could not have been determined by a skilled artisan without otherwise relying on the present application as a guide, which is improper. The patentability of the pending claims is further supported by the unexpected results shown in the present specification that are attributed to providing a MFI membrane having the claimed $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio.

For at least the foregoing reasons, Applicants respectfully submit that all claims pending herein define patentable subject matter over the applied references, and respectfully request that the above rejection be reconsidered and withdrawn.


If the Examiner believes that contact with Applicants' attorney would be advantageous toward the disposition of this case, the Examiner is herein requested to call Applicants' attorney at the phone number noted below.

The Commissioner is hereby authorized to charge any additional fees associated with this communication or credit any overpayment to Deposit Account No. 50-1446.

Respectfully submitted,

February 14, 2006

Date



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Attachments: Appendix A - substitute specification
Appendix B - marked-up specification

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DESCRIPTION

Laminated Zeolite Composite and
Method for Production Thereof

5

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation of International
Application No. PCT/JP02/09317 having an international filing
date of September 12, 2002, which designated the United
10 States, the entirety of which is incorporated herein by
reference.

This application also claims the benefit of Japanese
Application No. 2001-281675, filed September 17, 2001, the
entirety of which is incorporated herein by reference.

15

Technical Field

The present invention relates to a laminated zeolite
composite and a method for producing the laminated zeolite
composite.

20

Background Art

Zeolite composite membranes obtained by forming a
zeolite membrane on a substrate have been known and have been
used as a gas separation membrane or a liquid separation
25 membrane. With respect to such zeolite composite membranes,
it is known that when the $\text{SiO}_2/\text{Al}_2\text{O}_3$ (molar ratio) of the
membrane (hereinafter, it means a molar ratio when simply
"SiO₂/Al₂O₃" is mentioned) varies, the interaction between the
pore surface of zeolite and a molecule passing therethrough
30 varies and the characteristic of the membrane when used as a

separation membrane varies as well.

In, ~~for~~For example, p. 25 of an article by Yoji Sano and Yushi Kawakami in Kagaku Kogyo, Feb. 1995 ~~is~~
~~disclosed~~discloses a finding on the influence of $\text{SiO}_2/\text{Al}_2\text{O}_3$ on
5 the permeation and separation characteristic of MFI type
zeolite membrane (hereinafter referred to also as "MFI
membrane") when water and alcohol are separated from each
other by pervaporation using the membrane. It is known that
the membrane shows striking alcohol selectivity when the
10 $\text{SiO}_2/\text{Al}_2\text{O}_3$ thereof is increased.

As a specific example of the generally used MFI
membrane, there can be mentioned a zeolite composite membrane
obtained by forming a MFI membrane on an alumina substrate.
With respect to such a zeolite composite membrane, it is
15 known that, during the formation of the MFI membrane,
aluminum in the alumina-made substrate dissolves into the MFI
membrane and is taken into the skeleton of the MFI membrane
and, as a result, the MFI membrane becomes a $\text{SiO}_2/\text{Al}_2\text{O}_3$ -
reduced MFI membrane (hereinafter this membrane is expressed
20 also as "low-silica MFI membrane").

Also, ~~in~~ JP-A-6-127937 ~~are disclosed~~discloses a self-
supported MFI membrane not formed on any substrate
(hereinafter this membrane is ~~expressed as~~referred to as a
"MFI self-supported membrane"), into which aluminum is taken
25 and wherein the $\text{SiO}_2/\text{Al}_2\text{O}_3$ is reduced~~7,~~ and a method for the
production thereof.

In the zeolite composite membrane obtained by forming a
MFI membrane on an alumina substrate, however, it is
impossible to strictly control the $\text{SiO}_2/\text{Al}_2\text{O}_3$ of the MFI
30 membrane ~~strictly~~ and, therefore, it is difficult to steadily

synthesize a low-silica MFI membrane exhibiting uniform separation characteristic. Further, in synthesis of the MFI membrane, a structure-directing agent is added generally and it is necessary to remove the structure-directing agent by high-temperature calcination; however, since the substrate alumina and the MFI membrane (zeolite) differ in thermal expansion coefficient, the MFI membrane may generate cracks during calcination.

In the zeolite membrane described in JP-A-6-127937, since it is a MFI self-supported membrane, ~~there can be avoided~~ problems such as crack generation in MFI membrane due to difference in thermal expansion coefficient between substrate and zeolite can be avoided. Even in the method for the production of MFI membrane according to the above literature, however, it is described therein that the MFI membrane formed at the initial stage of synthesis has a large $\text{SiO}_2/\text{Al}_2\text{O}_3$ and the $\text{SiO}_2/\text{Al}_2\text{O}_3$ tends to become smaller with the growth of the membrane; therefore, a low-silica MFI membrane having small value in $\text{SiO}_2/\text{Al}_2\text{O}_3$ is obtainable only when the thickness of the membrane is made large. Consequently, the MFI membrane obtained exhibits permeation and separation characteristic as a low-silica MFI membrane, but has a large thickness and accordingly a small permeation factor and has a problem of low permeability.

The present invention has been made in view of such problems possessed by the prior art, and aims at providing a laminated zeolite composite having high separation ~~characteristic~~characteristics and a high permeability, and a method for producing such a laminated zeolite composite.

~~Disclosure~~Summary of the Invention

According to the present invention, there is provided a laminated zeolite composite characterized in that it comprises a MFI membrane ~~being constituted by a MFI type zeolite and having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ (molar ratio) of 40 to 100,~~ and a porous substrate ~~being constituted by a MFI type zeolite and having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ (molar ratio) of 20 to 400,~~ and that wherein the MFI membrane is formed on the porous substrate.

10 In the present invention, the MFI membrane preferably has a thickness of ~~preferably~~ 25 μm or less. Incidentally, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ (molar ratio) of the MFI membrane may gradually decrease from the side of the membrane contacting the porous substrate toward the other side thereof.

15 The laminated zeolite composite of the present invention is suitably used for the separation of butane isomers or for the separation of propane and propylene.

According to the present invention, there is also provided a method for producing a laminated zeolite composite comprising the steps of immersing a porous substrate in a silica sol-containing sol for membrane formation, and forming a MFI membrane on the porous substrate under heating conditions; ~~said the~~ method being characterized in that a porous substrate ~~being constituted by a MFI type zeolite and~~ having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ (molar ratio) of 20 to 400 is immersed in a sol for membrane formation having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ (molar ratio) in a range of 40 to 150 and a $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ (molar ratio) of 15 or less.

30 In the present invention, it is preferred to form a MFI membrane ~~being constituted by a MFI type zeolite and having a~~

SiO₂/Al₂O₃ (molar ratio) of 40 to 100.

Brief Description of the Drawings

Fig. 1 is a schematic drawing showing a mode for
5 carrying out the permeation and separation test of butane
isomers.

____ Fig. 2 is a graph wherein the separation factor of
butane isomers is plotted against the SiO₂/Al₂O₃ of MFI
membrane.

10

~~Best Mode for Carrying Out~~ Detailed Description of the Invention

Modes for carrying out the present invention are
described below. However, the present invention is not
15 restricted to the following modes and it should be construed
that design change, improvement, etc. may be made
appropriately based on the ordinary knowledge of those
skilled in the art as long as there is no deviation from the
gist of the present invention.

20 The first aspect of the present invention lies in a
laminated zeolite composite characterized in that it
comprises a MFI membrane ~~being~~ constituted by a MFI type
zeolite ~~and~~ having a SiO₂/Al₂O₃ (molar ratio) of 40 to 100,
and a porous substrate ~~being~~ constituted by a MFI type
25 zeolite ~~and~~ having a SiO₂/Al₂O₃ (molar ratio) of 20 to 400,
~~and that~~ wherein the MFI membrane is formed on the porous
substrate.

In the laminated zeolite composite of the present
invention, the SiO₂/Al₂O₃ of the MFI membrane may gradually
30 decrease from the side of the MFI membrane ~~contacting in~~ in

contact with the porous substrate toward the other side of
the MFI membrane. Incidentally, the term "gradually
decrease" ~~refers to~~means that the $\text{SiO}_2/\text{Al}_2\text{O}_3$ decreases
gradually within a range of 40 to 100. The details of the
5 first aspect are described below.

The present invention has been completed based on a
finding that there is a correlation between the $\text{SiO}_2/\text{Al}_2\text{O}_3$ of
MFI membrane and the separation factor of butane isomers when
the MFI membrane is used. That is, the laminated zeolite
10 composite of the present invention obtained by forming a MFI
membrane having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 40 to 100, on a porous
substrate ~~being composed of~~ a MFI type zeolite and having a
 $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 20 to 400, has a characteristic of gas
separation, for example, separation of butane isomers.

15 In the above-mentioned ~~p. 25 of an article~~ by Yoji Sano
and Yushi Kawakami in Kagaku Kogyo, Feb. 1995 ~~is disclosed~~
the influence of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ of the MFI membrane on the
permeation and separation characteristic of the MFI membrane
in separation of water and alcohol, i.e. components
20 separation when the to-be-treated material is a liquid is
disclosed. It should be noted, however, that no mention is
made therein ~~on~~of the influence on the gas separation
characteristic when the to-be-treated material is a gas. The
correlation between the $\text{SiO}_2/\text{Al}_2\text{O}_3$ of the MFI membrane and the
25 characteristic of gas separation including separation of
butane isomers has been found for the first time in the
present invention.

Further, in the laminated zeolite composite of the
present invention, since ~~there a~~ MFI membrane is formed, on a
30 porous zeolite substrate, ~~composed of a zeolite, and since~~

the membrane ~~(MFI membrane)~~ is composed of the same zeolite as in the porous substrate, ~~there are avoided, during production or use of the composite,~~ inconveniences such as crack generation in MFI membrane due to difference in thermal expansion coefficient between the porous substrate and the MFI membrane are avoided during production or use of the composite, and the MFI membrane keeps its function at a satisfactory level.

Incidentally, the term " $\text{SiO}_2/\text{Al}_2\text{O}_3$ (molar ratio)" referred to in the present invention ~~is~~ represents a value obtained by a measurement using energy dispersive spectroscopy (EDS).

A MFI membrane having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ~~of below~~ less than 40 is not preferred because the MFI membrane tends to generate cracks on the surface. Meanwhile, a MFI membrane having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ~~of beyond~~ greater than 100 is not preferred because ~~the MFI membrane,~~ when used as a separation membrane the MFI membrane, hardly exhibits ~~its any~~ any unique gas separation ~~characteristic~~ characteristics. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ of the MFI membrane is preferably 45 to 90, more preferably 50 to 80 from the standpoint of providing superior performance as a separation membrane. In order to allow the MFI membrane to have a $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 40 to 100, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ of the porous substrate is preferably 20 to 400. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ of the porous substrate is more preferably 40 to 100, which is the same level as that in the MFI membrane.

In the laminated zeolite composite of the present invention, the MFI membrane preferably has a ~~thin~~ thickness of 25 μm or less, whereby the MFI membrane has high separation characteristic and excellent permeability. In

order for the MFI membrane to exhibit particularly excellent permeability, the thickness of the MFI membrane is preferably 17 μm or less, more preferably 13 μm or less. In the present invention, there is no restriction as to the lower limit of the thickness of the MFI membrane. It should be noted, however, that the lower limit is sufficient at 0.1 μm or more in view of, ~~for example,~~ the function the MFI membrane when used as a separation membrane and the practical producibility of the MFI membrane, for example.

As Examples of the shape of the laminated zeolite composite of the present invention, ~~there can be mentioned,~~ for example, include a bar shape, a pellet shape, a flat sheet shape, a tube shape, a monolithic shape and a honeycomb shape.

~~The laminated zeolite composite of the present invention, by~~ By utilizing ~~its~~ the advantages of having an excellent separation characteristic and permeability and the property of hardly generating cracks, etc., the laminated zeolite composite of the present invention can be suitably used as a separation membrane for carrying out the separation of butane isomers or the separation of propane and propylene.

Next, description is made ~~on~~ of the second aspect of the present invention, which is ~~The second aspect of the present invention lies in~~ a method for producing a laminated zeolite composite comprising the steps of immersing a porous substrate in a silica sol-containing sol for membrane formation, and forming a MFI membrane on the porous substrate under heating conditions. ~~and said~~ The method is characterized in that a porous substrate ~~being~~ constituted by a MFI type zeolite ~~and~~ having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ (molar ratio) of 20

to 400 is immersed in a sol for membrane formation having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ (molar ratio) of 40 to 150 and a $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ (molar ratio) of 15 or less. In the present invention, it is preferred that a MFI membrane ~~being~~ constituted by a MFI type zeolite and having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 40 to 100 is formed. The details of the second aspect are described below.

Incidentally, ~~when simply the term~~ " $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ " ~~is mentioned hereinafter, it means~~ refers to a molar ratio.

When ~~there is used a sol~~ is used for membrane formation having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ of ~~below~~ less than 40 or ~~beyond~~ more than 150, the obtained MFI membrane ~~obtained~~ is unable to have a $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 40 to 100. Even when ~~there is used a sol~~ is used for membrane formation having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 40 to 150, but when the sol has a $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ of ~~beyond~~ greater than 15, ~~there is formed a MFI membrane~~ is formed having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ of ~~below~~ less than 40, which is not preferred.

In order for the MFI membrane formed to reliably have a $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 40 to 100, it is preferred to use a sol for membrane formation having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 50 to 130, and it is more preferred to use a $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 55 to 120. It is also preferred to use a sol for membrane formation having a $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ of 13 or less, and it is more preferred to use a sol for membrane formation having a $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ of 10 or less. Incidentally, there is no particular restriction as to the lower limit of the $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ of the sol for membrane formation used in the present invention. It should be noted, however, that the lower limit may be 1 or more in view of, for example, the practical production conditions of laminated zeolite composite.

In the present invention, a porous substrate having a

SiO₂/Al₂O₃ of 20 to 400 is immersed in the sol for membrane formation. As the method for producing such a porous substrate, a known conventional method may be used. In an example, tetrapropylammonium hydroxide (TPAOH), a silica sol, NaAlO₂, etc. are mixed at desired SiO₂/Al₂O₃ and TPAOH/SiO₂ (molar ratio) ~~the~~ The resulting mixture is stirred and kneaded with heating, to vaporize water to obtain a dry gel ~~the~~ and the dry gel is ground to obtain a powder ~~the~~ The powder is formed by an appropriate forming method to obtain a formed article ~~and then~~ and then the formed article is subjected to, for example, a reaction under a steam pressure, whereby a porous substrate having a SiO₂/Al₂O₃ ~~of~~ in the desired range can be produced. Incidentally, as the appropriate forming method, ~~there may be used an~~ ordinary ceramic forming method such as extrusion forming, CIP forming, slip casting or the like may be used.

In the above example of the ~~production method of~~ method of producing the porous substrate, it is preferred to use NaAlO₂ as a Na and Al source. When the Na₂O/Al₂O₃ is larger than 1, the porous substrate obtained has crystalline Na separated thereon; when the Na₂O/Al₂O₃ is smaller than 1, the obtained porous substrate ~~obtained~~ has a ~~small~~ low strength. NaAlO₂ is preferred because it contains Na and Al ~~at~~ in a 1:1 (molar ratio) and the Na₂O/Al₂O₃ can be controlled strictly at 1.

The porous substrate produced by ~~for example~~ the above method for example, is immersed in the sol for membrane formation having a SiO₂/Al₂O₃ of 40 to 150 and a Na₂O/Al₂O₃ of 15 or less ~~a~~ A reaction is allowed to take place under a heating condition ~~thereby~~ and a MFI membrane

is thereby formed on the porous substrate. Here, the term "under a heating condition" refers to a reaction in a temperature range of 100 to 200°C in a pressure vessel.

The obtained membrane-formed substrate is ~~heated~~
5 appropriately heated to at about 500 to 600°C in, for example, an electric oven and ~~kept~~ held for about 4 to 10 hours at this temperature to remove the structure-directing agent (TPA) used. The ~~keeping~~ holding time and the heating and cooling ~~rate of temperature increase or decrease are~~
10 ~~determined~~ determined so as to match the sizes of membrane-formed substrate and electric oven. Incidentally, in the present invention, the thickness of the MFI membrane formed is preferably set at 25 µm or less, more preferably at 17 µm or less, particularly preferably at 13 µm or less.
15 Thereby, a laminated zeolite composite having high permeability can be obtained.

Incidentally, the thickness of the MFI membrane can be controlled ~~by~~, for example, by controlling the reaction time.

In the present invention, there is no restriction as to
20 the lower limit of the thickness of the MFI membrane formed. However, the lower limit is sufficient at 0.1 µm or more in view of, for example, the function of MFI membrane as a separation membrane and the practical producibility of the MFI membrane.

25 In the present invention, it is preferred to form a MFI membrane having a SiO₂/Al₂O₃ ratio of 40 to 100 because the MFI membrane can allow the resulting laminated zeolite composite to have a particularly excellent function as a separation membrane. In order for the MFI membrane to
30 exhibit a particularly excellent function as a separation

membrane, it is more preferred for the MFI membrane ~~is more preferred to have a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 45 to 90, and it is particularly preferred to have a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 50 to 80.~~

5 Examples

The present invention is specifically described below by way of Examples. However, the present invention is not restricted to these Examples.

10 ~~_____ (Examples 1 to and 2 and Comparative Examples 1 to 6)~~

~~1. Production method of porous~~ Method of producing substrate A

To 16.27 g of a 10% aqueous TPAOH solution (a product of Wako Pure Chemical Industries, Ltd.) were added 0.656 g of NaAlO_2 (a product of Wako Pure Chemical Industries, Ltd.) and
15 40.05 g of about 30wt% silica sol (Snowtex S, a product of Nissan Chemical Industries, Ltd.). The mixture was stirred at room temperature for 1 hour using a desk shaker and then stirred and kneaded with heating at about 80°C using a hot stirrer, to vaporize water, whereby a colorless dry gel was
20 obtained.

The dry gel was ground to obtain a powder, after which the powder was subjected to uniaxial pressing with a die at a total pressure of 2 ton to obtain a formed article having a disc shape having a diameter of 19 mm and a thickness of 2 mm.
25 The formed article was set on a fluororesin plate in a stainless steel-made pressure vessel with a fluororesin-made inner cylindrical container placing distilled water of the same weight as the formed article, in a state that there is no contact between the formed article and the water. After
30 the pressure vessel was placed in an oven of 180°C , the

contents of the vessel ~~was~~were subjected to a reaction under a self steam pressure for 12 hours, whereby a porous substrate (porous substrate A) was obtained.

The crystal phase of the obtained porous substrate A
5 ~~obtained~~ was examined by X-ray diffractiometry. As a result, ~~the~~ porous substrate A was found to be an MFI type zeolite of perfect crystal. Incidentally, ~~as to the~~ crystal phase of zeolite, ~~a case when, in the~~ X-ray diffractiometry, ~~there was~~ showed only a broad halo and no clear peak ~~were found~~, in a
10 region of 20 to 30° (CuK α), was expressed as "amorphous"; ~~a case~~ when a zeolite peak was seen even slightly, the crystal phase was expressed as "under crystallization"; and ~~a case~~ when all sharp peaks of zeolite were seen clearly and there was no halo, the crystal phase was expressed as a "perfect
15 crystal." Incidentally, the SiO₂/Al₂O₃ of the porous substrate A was 50.

2. ~~Production method of~~ Method of producing porous substrate B

To 16.27 g of a 10% aqueous TPAOH solution (a product
20 of Wako Pure Chemical Industries, Ltd.) was added 40.05 g of about 30wt% silica sol (Snowtex S, a product of Nissan Chemical Industries, Ltd.). The mixture was stirred at room temperature for 1 hour using a desk shaker and then stirred and kneaded with heating at about 80°C using a hot stirrer,
25 to vaporize water, whereby a colorless dry gel was obtained. The later operation was conducted in the same manner as in production of the porous substrate A, to obtain a porous substrate (porous substrate B).

The crystal phase of the obtained porous substrate B
30 ~~obtained~~ was examined by X-ray diffractiometry. As a result,

the porous substrate B was found to be an MFI type zeolite of perfect crystal. Incidentally, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ of the porous substrate B was 500 or more.

5 3. Formation of MFI membranes

There were mixed, so as to give compositions shown in Table 1, various raw materials, i.e. a 10% aqueous TPAOH solution (a product of Wako Pure Chemical Industries, Ltd.), distilled water, tetrapropylammonium bromide (a product of Wako Pure Chemical Industries, Ltd.), aluminum sulfate (14 to 18 hydrates) (a product of Wako Pure Chemical Industries, Ltd.), a 30wt% silica sol (Snowtex S, a product of Nissan Chemical Industries, Ltd.) and a 4N aqueous sodium hydroxide solution (a product of Wako Pure Chemical Industries, Ltd.).

15 The mixture was stirred at room temperature for 60 minutes using a desk shaker to produce a sol for membrane formation. The sol for membrane formation was placed in a 100ml-stainless steel-made pressure vessel with a fluororesin-made inner cylindrical container. Therein was immersed one of the

20 above-produced porous substrates A or B. After the pressure vessel was placed in an oven of 180°C , the contents of the vessel ~~was~~were subjected to a reaction for 8 hours, whereby a MFI membrane was formed on the porous substrate. The resulting membrane-formed substrate was placed in an

25 electric oven, the substrate temperature was elevated to 550°C and then ~~kept~~held at this temperature for 4 hours to remove the TPA, whereby the laminated zeolite composites ~~were produced of~~ (Examples 1 to 2 and Comparative Examples 1 to 6) were produced.

30 Incidentally, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ of each sol

for membrane formation and the $\text{SiO}_2/\text{Al}_2\text{O}_3$ of each porous substrate are shown in Table 2.

Table 1

	10% tetrapropylammonium hydroxide solution (g)	Distilled water (g)	Tetrapropyl ammoniumbro mide (g)	Aluminum sulfate (g)	30wt% silica sol (g)	4N aqueous sodiumhydroxi de solution (g)	Porous substrate
Exam. 1	15.26	49.85	0	0.21	6	1	A
Exam. 2	15.26	49.85	0	0.21	6	2	A
Comp. Exam. 1	15.26	49.85	1.995	0	6	0	B
Comp. Exam. 2	15.26	49.85	0	0.21	6	1	B
Comp. Exam. 3	15.26	49.85	0	0.21	6	3	B
Comp. Exam. 4	10.17	49.85	1.995	0.21	6	1.6	B
Comp. Exam. 5	15.26	49.85	1.995	0	6	0	A
Comp. Exam. 6	15.26	49.85	0	0.21	6	3	A

Table 2

	Sol for membrane formation		SiO ₂ /Al ₂ O ₃ (molar ratio) of porous substrate
	SiO ₂ /Al ₂ O ₃ (molar ratio)	Na ₂ O/Al ₂ O ₃ (molar ratio)	
Exam.1	40 to 150	<15	50
Exam.2	40 to 150	<15	50
Comp.Exam.1	>150	-	>500
Comp.Exam.2	40 to 150	<15	>500
Comp.Exam.3	40 to 150	>15	>500
Comp.Exam.4	40 to 150	<15	>500
Comp.Exam.5	>150	-	50
Comp.Exam.6	40 to 150	>15	50

_____ {Evaluation of MFI membranes (separation membranes)}

5

1. Thickness measurement and surface observation of each MFI membrane

By observing the cross-section and surface of each MFI membrane using a SEM, the thickness of each MFI membrane was measured and the crack generation of cracks at the surface of each MFI membrane was examined. ~~A case when~~When cracks were confirmed by the SEM observation, the sample was rated as "present," and ~~a case when~~ no cracks were confirmed, the sample was rated as "not present."

15

The thickness of each MFI membrane formed on each laminated zeolite composite was 15 to 25 μm . The result of examination of the generation of cracks at the surface of each MFI membrane is shown in Table 3.

20

2. Determination of SiO₂/Al₂O₃

The SiO₂/Al₂O₃ ratio of MFI membrane was determined by EDS. The determination of the SiO₂/Al₂O₃ ratio of the MFI

membrane according to EDS was carried out by scanning the whole surface of the cross section of the MFI membrane. The results thereof are shown in Table 3.

5 3. Permeation and separation test

A permeation and separation test for butane isomers was carried out by the Wicke-Kallenbach method. Fig. 1 schematically shows a mode for carrying out the permeation and separation test for butane isomers. Fig. 1 shows a state
10 in which there is placed, inside a permeation and separation test apparatus 10, a separated gas-holding unit 12 fitted with a laminated zeolite composite 11. Incidentally, the permeation and separation test apparatus 10 is heatable by an electric oven 13.

15 A mixed gas containing about 5% by volume of isobutane and about 5% by volume of normal butane (n-butane) was fed to one side of the laminated zeolite composite 11 using a N₂ gas as a carrier gas, under a heating condition of 200°C, and the gas after permeation, at the opposite side of the laminated
20 zeolite composite was swept by a N₂ gas and analyzed by gas chromatography. The separation factor of butane isomers is shown in Table 3. Incidentally, the separation factor of butane isomers is a value determined by the following expression—(1)—, wherein X_n and X_{iso} are, respectively, the
25 molar concentrations of n-butane and isobutane at the supply side of the gas, and Y_n and Y_{iso} are, respectively, the molar concentrations of n-butane and isobutane at the permeation side of the permeated gas—:

30 Separation factor of butane isomers = $(Y_n/Y_{iso}) / (X_n/X_{iso})$.—

(1)

Table 3

	Crack generation at surface of MFI membrane	SiO ₂ /Al ₂ O ₃ (molar ratio) of MFI membrane	Separation factor of butane isomers
Exam.1	Not present	52	84.3
Exam.2	Not present	79	62.0
Comp.Exam.1	Not present	225	16.0
Comp.Exam.2	Not present	130	16.3
Comp.Exam.3	Present	26	19.8
Comp.Exam.4	Not present	107	14.2
Comp.Exam.5	Not present	201	11.7
Comp.Exam.6	Present	29	14.2

5

In Fig. 2 is shown a graph in which showing the separation factor butane isomers are plotted against the SiO₂/Al₂O₃ value of each MFI membrane.

10 (Discussion)

In order to produce a laminated zeolite composite exhibiting excellent separation characteristics, it is required that (1) the porous substrate used has a SiO₂/Al₂O₃ of 20 to 400, (2) the sol used for the membrane formation has a SiO₂/Al₂O₃ of 40 to 150, and (3) the sol used for the membrane formation has a Na₂O/Al₂O₃ of 15 or less. Explanation is made below on each Example and each Comparative Example, based on the results obtained above.

20 In Example 1, the porous substrate had a SiO₂/Al₂O₃ of 50 and the sol used for the membrane formation had a SiO₂/Al₂O₃ of 95 and a Na₂O/Al₂O₃ of 6.3, and all of the above requirements (1) to (3) for producing a laminated zeolite composite exhibiting excellent separation

characteristic ~~are~~were satisfied. In Example 2, the porous substrate had a $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 50 and the sol used for the membrane formation had a $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 95 and a $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ of 12.6, and all of the above requirements (1) to (3) for
5 ~~production of~~producing a laminated zeolite composite exhibiting excellent separation characteristic ~~are~~were satisfied.

Meanwhile, in Comparative Examples 1 to 4, ~~the~~ porous substrate B having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ of >400 was used and ~~the~~
10 requirement (1) ~~is~~was not satisfied. Further, in Comparative Example 1, ~~at~~the sol used for the membrane formation ~~having had~~ a $\text{SiO}_2/\text{Al}_2\text{O}_3$ of >150 ~~was used and the~~ requirement (2) ~~is~~was not satisfied. In Comparative Example 3, ~~at~~the sol used for the membrane formation ~~having had~~ a $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ of 18.9 ~~was~~
15 ~~used and the~~ requirement (3) ~~is~~was not satisfied.

In Comparative Examples 5 and 6, ~~the~~ porous substrate A having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 50 was used and ~~the~~ requirement (1) ~~is~~was satisfied. However, in Comparative Example 5, ~~at~~the sol used for the membrane formation ~~having had~~ a $\text{SiO}_2/\text{Al}_2\text{O}_3$ of >150
20 ~~was used and the~~ requirement (2) ~~is~~was not satisfied ~~and~~.
~~in~~In Comparative Example 6, ~~at~~the sol used for the membrane formation ~~having had~~ a $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ of 18.9 ~~was used and the~~ requirement (3) ~~is~~was not satisfied.

It is clear from the results of Table 3 and Fig. 2 that
25 Examples 1 and 2, compared with Comparative Examples 1 to 6, each show a very high separation factor for n-butane and isobutane. That is, it is clear that the laminated zeolite composites of Examples 1 and 2, as compared with those of Comparative Examples 1 to 6, each have excellent separation
30 ~~characteristic~~characteristics and hardly generate

inconveniences such as cracks on the MFI membranemembranes.

Incidentally, the laminated zeolite composites of Examples 1 and 2, as compared with those of Comparative Examples 1 to 6, showed a high separation factor of about 1.5
5 times, also in separation of propane and propylene.

Industrial Applicability

As described above, in the laminated zeolite composite of the present invention, the MFI membrane and the porous
10 substrate each have a $\text{SiO}_2/\text{Al}_2\text{O}_3$ efin a given range and the MFI membrane is formed ~~inat~~ at a given thickness on such a porous substrate. Therefore, the present laminated zeolite composite has high separation ~~characteristic~~characteristics and high permeability and can be suitably used~~in~~, for
15 example, in the separation of butane isomers or of propane and propylene.

According to the present method for producing a laminated zeolite composite, since a porous substrate having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ efin a given range is immersed in a sol used for
20 the membrane formation having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ efin a given range, the MFI membrane formed can easily have a $\text{SiO}_2/\text{Al}_2\text{O}_3$ efin a predetermined range.